Synthesis, Characterization, and Structure Determination of Bis-oxazolidine Complexes of Rhenium

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ARTICLE

Synthesis, Characterization, and Structure Determination of Bis-oxazolidine Complexes of Rhenium

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A tetradentate fused bis-oxazolidine ligand (FOX) is used to coordinate to rhenium carbonyl. The ligand binds in a κ^3-*NNN* fashion to a $Re(CO)_3^+$ fragment, giving an octahedral complex. The hydroxymethyl group can be deprotonated with CsOH, leading to a κ^3-*ONN* variation in the binding of the ligand. Loss of CO from this compound proved difficult, impeding further reactivity.

1. Introduction

In recent decades, investigations of rhenium complexes and their applications to homogeneous catalysis has offered new approaches to an array of organic reactions.[1] A common subset of rhenium complexes are the rhenium tricarbonyls, which have demonstrated catalytic activity in several C–C and C–X (X = Si, N, O, S, Se) bond forming reactions, reductive processes, and photochemical transformations.[2] Recently, Re(I) tricarbonyl complexes supported by PNP or bipyridine (bpy) ligands were found to be catalytically active in the *N*-alkylation of anilines,[3] hydrogenation of carbonyl derivatives,[4] coupling of C_1 and C_2 alcohols,[5] and reduction of CO_2[6-8] (Figure 1).

Mechanistic insights into these systems determined the ligands' role in catalysis through the acid/base properties of central N-atom of a PNP ligand or redox profile of bpy. In the case of the former, a non-innocent central atom metal fixes the ligand's coordination geometry and supports catalysis; the N-atom of complexes **1** and **2** facilitates proton transfer between catalyst and substrate. The bpy ligand of complex **3** participates in electron transfer processes and can temporarily store an electron in the form of a radical that is stabilized through resonance delocalization.

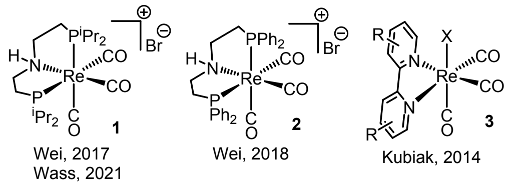
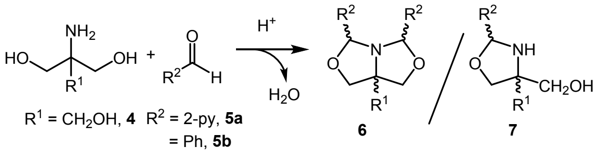


Figure 1. Examples of rhenium *fac*-tricarbonyl catalysts.

Our group has recently prepared a series of first-row metals bearing chelating fused oxazolidine (FOX) ligands, which exhibit a diversity of coordination modes.[9] In consideration of the activity of these structurally similar, tris-chelating ligands on rhenium(I) tricarbonyls, we set out to synthesize a $Re(FOX)(CO)_3$ complex and explore its catalytic profile.

1.1 Introduction to Fused Oxazolidine (FOX) Ligands

Fused oxazolidine ligands were first synthesized by Senkus in 1945 by condensation of N-dialkylamino alcohols with aldehydes (eq 1). Both monocyclic and fused bicyclic oxazolidines were prepared in the initial report. Several derivatives were prepared therein as well as in the several decades since, usually by the same method used by Senkus.[10-16] Containing a backbone related to pyrrolizidines that are known to naturally occur and possess biological activity,[17] FOX compounds have displayed bioactivity as chemotherapeutics[18] and biocides.[19] Controlling the stereochemistry in the synthesis of FOX compounds is challenging, yet important, to applications in coordination chemistry and biologic systems. Generally, they are obtained as a mixture of diastereomers which may be resolved by column chromatography (Figure 2).[13]



(1)

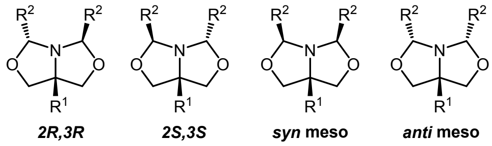


Figure 2. Stereochemistry of FOX Compounds.

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† Electronic Supplementary Information (ESI) available: Includes NMR spectra and details of the X-ray structures of **8** and **10** (2 polymorphs. These data are available from the Cambridge Structural Database (CCDC #2262446-2262448). See DOI: 10.1039/x0xx00000x

Computational[20] and experimental[21] evidence suggests the first step in the formation of FOX bicycles is an imine condensation that occurs by nucleophilic attack of the amine N-atom (**4**) on aldehyde (**5**) to give a racemic mixture of monocyclic products of type **7** (eq 1). The second cyclization, which determines the stereochemistry of the product mixture, may occur either by nucleophilic attack of a hydroxyl O-atom or 2°-amine N-atom on another molecule of **5**. Computational evidence obtained by density functional theory (DFT) calculations suggest the that the *anti* meso conformation is higher in energy than its *syn* meso form when **4** is reacted with **5b** ($\Delta E \approx 12$ kcal·mol^{-1}), while the corresponding chiral *R,R* and *S,S* compounds are disfavored by ~2 kcal·mol^{-1}.[13] These calculations account for the general experimental absence of *anti* meso products. A kinetic analysis on the reaction of **4** and **5a** in methanol revealed the chiral isomers are kinetically preferred over their meso diastereomers as they are the major products observed after 1 h at 65 °C. One contributor to diastereoselectivity is the steric environment enforced by R^2 during ring formation.[12]

It was previously demonstrated that the chiral *R,R* and *S,S* FOX bicycles can be isomerized to the *syn* meso compound through a templating Lewis acid such as $FeCl_3$ or $AlCl_3$ in the case that R^1 = CH_2OH and R^2 = 2-pyridine.[9] This transformation is thought to occur through an acid-catalyzed ring-chain-ring tautomerization, similarly to thiazolidinyloxazolidine compounds in which one oxygen atom in the bicycle is replaced with sulfur.[22] Direct synthesis of the *syn* meso compounds from pyridine-2-carbaldehyde and TRIS precursors was achieved by Darabantu et al. using benzene as solvent and catalytic amounts (1-5 mol %) of *p*-toluenesulfonic acid (PTSA).[13] However, it was determined that the fused oxazolidine ring system is sensitive to hydrolysis in acidic media.[12] Consequentially, there are associated challenges in recrystallization from alcoholic solvent[12] and purification by column chromatography on a silica stationary phase[13] since the product is prone to decomposition. Thus, the utility of Lewis acids for the isomerization of chiral FOX species to the corresponding meso compounds was demonstrated. The variability in the coordination geometry of the FOX ligands generated by reaction of **4** and **5a** (**L1**$^{\mathbf{rac}}$ and **L1**$^{\mathbf{meso}}$) is highlighted in Figure 3.[9]

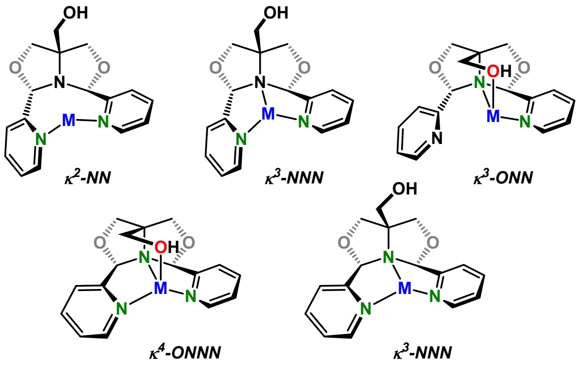

Figure 3. Common Coordination Modes of **L1**$^{\mathbf{rac}}$ (Top) and **L1**$^{\mathbf{meso}}$ (Bottom).

1.2 FOX Ligands in catalysis

In the past decade, several transition metal complexes bearing FOX ligands have been prepared, and some have been used as homogenous catalysts. In 2010, Shi et. al reported a Cu^I(FOX)-catalyzed asymmetric propargylation of ketones.[23] Five years later, A Cu^{II}(FOX) complex (R^1 = CH_2OH, R^2 = 2-pyridine) was deposited into the Cambridge Structural Database (CSD).[24] Later that year, Zhang et. al. reported the *in-situ* generation of a FOX-ligated lanthanide complex bearing the 8-hydroxyquinoline moiety at the R^2 position by introducing TRIS and the appropriate aldehyde to a solution of cerium^{III} chloride hexahydrate.[25] An oxo-bridged, dinuclear Fe^{III}(FOX) complex (R^1 = CH_2OH, R^2 = 2-pyridine) was found to electrochemically catalyze the oxidation of water to molecular oxygen in a report by Karim et. al in 2020.[26] The series of first-row metals (Mn, Fe, Co, Ni, and Cu) supported by FOX ligands was expanded by Nachtigall et. al's 2021 findings, wherein 22 complexes were prepared with substituted pyridines at the R^2 position.[9] The $[Fe^{II}(OTf)_2(FOX)]$ complex was found to selectively dehydrate 1-phenylethanol to styrene in good yields and with low catalyst loading.[25] Recently, Cu^{II}(FOX) complexes (R^1 = CH_2OH or Et, R^2 = 2-pyridine) were found to catalyze the production of β-hydroxy-1,2,3-triazoles from sodium azide, phenylacetylene, and epichlorohydrin in water with high yield and selectivity.[16] Late d-block transition metal FOX complexes have not been previously reported. In this report, new rhenium complexes of the FOX^{meso} ligand are explored.

2. Results and discussion

2.1 Complex Synthesis and Characterization

Preparation of the FOX ligands used in this work was achieved by using a modified literature procedure (see ESI).[9] Each ligand features the fused oxazolidine backbone of **7**, with R^1 = CH_2OH and an ortho-substituted pyridyl substituent at R^2 (Figures 2, 4). For simplicity, these ligands will henceforth be referred to by **L1**, **L2**, and **L3**, with superscripts to differentiate the chiral enantiomers ("rac") from the *syn* meso ("meso") diastereomer. The synthetic approach to these compounds followed the common strategy of adding two equivalents of aldehyde to a methanolic solution of TRIS in the presence of catalytic amounts of acid, and heating to 65 °C. Here, acetic acid was used as the catalyst. Racemic mixtures of the ligands are obtained selectively as **L1**$^{\mathbf{rac}}$, **L2**$^{\mathbf{rac}}$, and **L3**$^{\mathbf{rac}}$ after purification by recrystallization. To isomerize the enantiomers to their syn meso diastereomers, catalytic quantities of $AlCl_3$ (a templating Lewis acid) was added to solution of the chiral compounds in acetonitrile at elevated temperature. Pure quantities of **L1**$^{\mathbf{meso}}$, **L2**$^{\mathbf{meso}}$, and **L3**$^{\mathbf{meso}}$ in crystalline form were obtained through

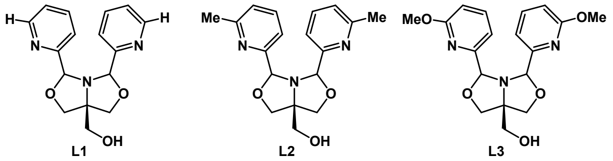

Figure 4. Selected FOX Ligands.

subsequent purification by column chromatography and recrystallization.

The compound *fac*-[Re(**L1**^{meso})(CO)$_3$]Br (**8**) was then synthesized in moderate yield by heating a solution of Re(CO)$_5$Br and **L1**^{meso} in toluene. Recrystallization of the crude solid was achieved by diffusion of hexanes into a solution of the crude product in dichloromethane (DCM), which gave colorless blocks that were analyzed by single crystal X-ray diffraction. Details of the structure solution and refinement are available in the ESI. The ligand adopts a facial, κ^3–*NNN* binding mode on the metal and the compound crystallizes as a distorted octahedron in the monoclinic space group $P2_1/n$ (Figure 5). The bromide counterion is hydrogen-bonded to the hydroxymethyl group. The observed rhenium-carbonyl bond lengths of 1.923(4)–1.938(4) Å in **8** are consistent with those in the structurally similar [Re(L)(CO)$_3$]Br (L = bis(pyridin-2-ylmethyl)amine) complex (**9**), where the observed Re−C$_{CO}$ bond lengths were 1.901(6)–1.926(7).[27] The observed Re−Namine and Re−NPy bond lengths in **8** were within 0.03 Å of those in **9** (Table 1). The ^{1}H NMR spectrum of **8** showed a downfield shift of the resonances associated with the **L1**^{meso} compared to the free ligand, as well as two distinct ^{13}C NMR signals at δ = 194.78 and 195.15 assigned to the carbonyls. The latter is an expected result considering the C$_s$ symmetry of the complex. The structure assignment is further supported by 2D NMR experiments COSY and ^{1}H−^{13}C HSQC, with all expected correlations observed. Metalation of **L2**^{meso} and **L3**^{meso} by reaction with Re(CO)$_5$Br under thermal and photochemical conditions was unsuccessful. (see ESI)

Table 1. Comparison of Selected Bond Lengths (Å) and Chemical Shifts (δ) of Rhenium tricarbonyl Complexes.

Compound	Re(CO)$_5$Br	**8**	**9**[27]	**10**
Re-CO	1.933(7) - 2.025(5)[28]	1.923(4) - 1.938(4)	1.901(6) - 1.926(7)	1.905(4) - 1.926(4)
Re-N$_{Py}$	-	2.169(3) - 2.171(3)	2.177(5) - 2.183(5)	2.197(3)
Re-N$_{amine}$	-	2.245(3)	2.187(4)	-
δ(CO)	178.39[a]	194.78, 195.15[b]	-	not obs.
δ(C(4)-H)	-	6.31[b]	-	7.09[c]
δ(C(6)-H)	-	6.31[b]	-	5.56c[c]

[a]CDCl$_3$. [b]CD$_3$CN. [c]THF-d_8.

2.2 Catalytic Activity Probe

In consideration of the demonstrated ability of complex **1**, of type [Re(PNP)(CO$_3$)]$^+$, to couple ethanol (EtOH) and methanol (MeOH) to selectively produce ^{i}BuOH,[5] the structurally similar complex **8** was tested for its ability to catalyze the transformation. The results are shown in Table 2. Beginning with the conditions optimized in King et. al's 2018 work (entry 1), no C$_4$-OH was detected by GCMS. A similar result was obtained after an increase in the catalyst loading (entry 2), and heating for an additional 5 h (entry 3). As previous studies[3,5] have suggested the active catalyst is formed by dissociation of a carbonyl ligand, trimethylamine N-oxide (TMANO) was added (entries 4 and 5) to promote decarbonylation of **8** by loss of CO$_2$.[29] In the absence of product formation, an alternative method was used to facilitate catalyst activation, namely photochemically induced dissociation of the carbonyl ligand by UV irradiation (entry 6).[30] Post-reaction GCMS analysis revealed only the starting alcohols. These findings led us to further derivatize the complex (**8**) to promote catalytic activity.

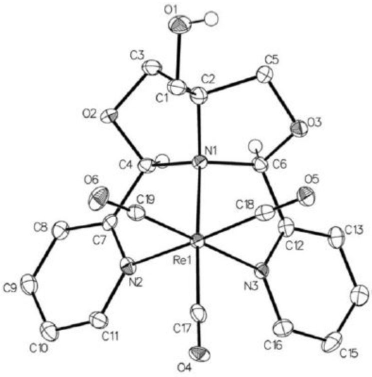

Figure 5. ORTEP of *fac*-[Re(L1^{meso})(CO)$_3$]Br (8). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å): Re(1)-N(1), 2.245(3); Re(1)-N(2), 2.171(3); Re(1)-N(3), 2.169(3); Re(1)-C(17), 1.923(4); Re(1)-C(18), 1.933(4); Re(1)-C(19), 1.938(4).

Table 2. Catalytic Upgrading of EtOH to ^{i}BuOH.

$$2\ \mathrm{MeOH} + \mathrm{EtOH} \xrightarrow[\mathrm{NaOMe\ (200\ mol\%)}]{[\mathrm{Re}(\mathbf{L1}^{meso})(\mathrm{CO})_3]\mathrm{Br}} {}^{i}\mathrm{BuOH}$$

entry	EtOH, mmol	[Re], mol%	*T*, °C	time, h	additive	C$_4$OH[a]
1	25	0.08	175	19	-	no
2	25	1	180	18	-	no
3	4.6	0.6	160	24	-	no
4	4.6	5	165	46	TMANO, 10 mol%	no
5	4.6	5	175	70	TMANO, 10 mol%	no
6	4.6	5	22	24	*h*ν	no

[a]determined by GCMS

2.3 Complex Derivatization

Sources of hydride (H–) have been used in the synthesis of metal formyl complexes from metal carbonyls.[31] Metal formyl complexes commonly decompose to give a metal hydride complex with loss of CO.[32] When **8** was reacted with one equivalent of potassium triethylborohydride (KBHEt$_3$), the neutral κ^3–*ONN* complex **10** was formed through deprotonation of the pendant alcohol on the ligand followed by substitution, rather than formation of the formyl complex. This coordination mode (i.e., deprotonation) has not heretofore been observed for **L1**^{meso}. A single crystal X-ray structure of the colorless blocks obtained by layering a tetrahydrofuran (THF) solution of the crude solid product with hexanes was obtained (Figure 6). It was determined that the compound crystallizes as a distorted octahedron in the triclinic space group *P*-1.[33] Additional details of the structure solution and refinement are available in the ESI. ^{1}H NMR analysis of **10** shows distinct resonances for nearly all aromatic protons, as the signal for two such nuclides overlap, which is consistent with the reduced symmetry of the complex relative to **8**. Methinyl protons bound to C(6) and C(4) generated distinct and well resolved signals (Δδ = 1.53 ppm), further supporting reduced symmetry in **10** (Table 1). A distinct signal was observed for each pyridyl carbon in the ^{13}C NMR spectrum, and the expected couplings were observed in the 2D NMR experiments COSY and ^{1}H–^{13}C HSQC. The complex **10** was also formed when **8** was treated with CsOH in THF.

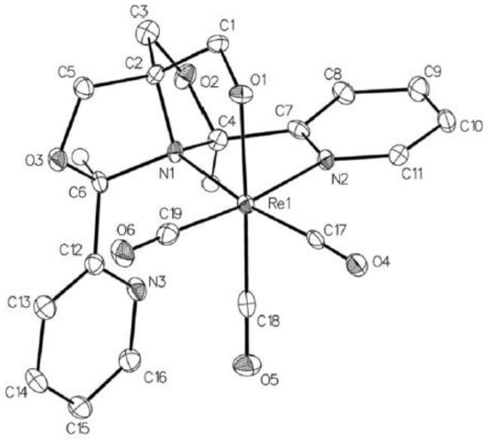

Figure 6. ORTEP of *fac*-Re(L1^{meso-H})(CO)$_3$ (**10**). Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å): Re(1)-N(1), 2.234(3); Re(1)-N(2), 2.197(3); Re(1)-O(1), 2.110(2); Re(1)-C(17), 1.905(4), Re(1)-C(18), 1.926(4); Re(1)-C(18), 1.926(4).

Previous studies found that triphenylphosphine (PPh$_3$) can displace CO ligands from M(CO)$_5$X (M = Mn, Re; X = Cl, Br, I).[34,35] In an attempt to substitute the carbonyl ligands on **10**, the complex was treated with TMANO in the presence of PPh$_3$ at 50 °C in THF over 17.5 h (see ESI). ^{1}H and COSY NMR spectra of the crude reaction mixture repeatedly showed starting **10** and free phosphine. X-ray diffraction analysis of solids crystallized from the reaction mixture also gave the structure of **10**. Substitution of the carbonyl ligands was not achieved using these conditions.

2.3 Electrochemical Investigation.

The electrochemistry of **10** was investigated in THF solution with tetrabutylammonium hexafluorophosphate electrolyte. Under argon atmosphere, compound **10** showed a single irreversible reduction at -2.70 V. When the argon was replaced with a CO$_2$ atmosphere, a doubling of the current was observed, suggestive of CO$_2$ reduction (Fig. 7). Addition of 0.1 M PhOH showed only a slight current increase. Similar behavior was seen in acetonitrile solution. A second sample of **10** in acetonitrile (1 mM) under an atmosphere of CO$_2$ with 1 M PhOH was subjected to controlled potential electrolysis (CPE) at -2.1 V for 60 min in a sealed cell with ~2 mL overhead volume. 3.59 C of charge were passed. The gas was sampled and found to contain CO. Using added methane as an internal standard, the CO was roughly quantified as 25% based upon the amount of **10** present. Consequently, **10** does not appear to be efficient for the catalytic CO$_2$ reduction to CO (8% Faradaic efficiency).

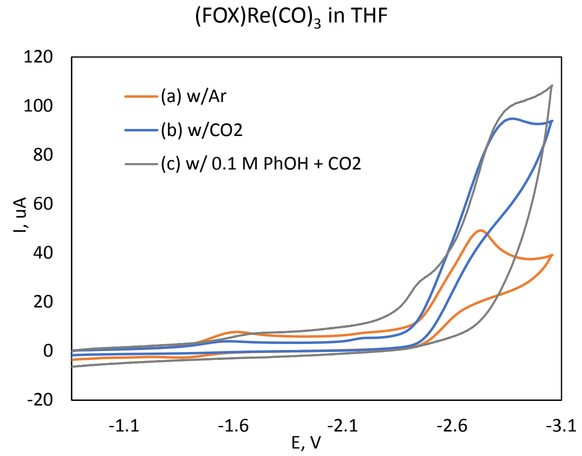

Figure 7. CV of 1 mM *fac*-Re(L1^{meso-H})(CO)$_3$ (**10**) in THF solution containing tetrabutylammonium hexafluorophosphate (0.1 M) under (a) argon, (b) CO$_2$, and (c) 0.1 M PhOH + CO$_2$ atmosphere. Values are referenced to added ferrocene (@ 0.0 V).

3. Experimental

3.1 General Procedures.

Unless otherwise specified, all reagents were used directly as purchased from Aldrich, Fisher, or Acros except for dichloromethane (DCM) which was used as received from Mallinckrodt. Tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were distilled from sodium metal and benzophenone. Acetonitrile (MeCN) was distilled from phosphorus pentoxide. Toluene and hexanes were purified by passage through a column of activated alumina. ^{1}H and ^{13}C{^{1}H} NMR data were recorded on 400 MHz and 500 MHz Bruker Avance NMR spectrometers. NMR assignments are made using chemical shifts, multiplicities, and correlations in the 2D NMR experiments ^{1}H–^{13}C HSQC and COSY. ESI-MS spectra were obtained on an Advion LCMS. A Rigaku Synergy-S diffractometer with dual PhotonJet-S microfocus X-ray sources (Cu Kα, Mo Kα) and a HyPix-6000HE HPC detector was used for crystallographic experiments. The ligands **L1^{meso}**, **L2^{meso}**, and **L3^{meso}** were synthesized as previously reported.[9]

3.2 Synthesis of *fac*-[Re(L1^{meso})(CO)$_3$]Br (8).

A flame-dried 100-mL round bottom flask was charged with Re(CO)$_5$Br (1.42 g, 3.49 mmol), **L1^{meso}** (1.13 g, 3.77 mmol, 1.08 equiv), and a Teflon-coated stir bar. Toluene (50 mL), purified before use by passage over a column of activated alumina, was then introduced to the flask. The mixture was sparged with N$_2$ for 15 minutes before a water-cooled condenser was affixed to the flask. The headspace was purged with N$_2$ for an additional 10 minutes. While stirring under slow N$_2$ flow, the contents of the flask were heated to 110 °C in an oil bath. After 74.5 h, a white precipitate was present at the bottom of the now golden-colored solution, which was collected by suction filtration and dried in vacuo (crude yield 2.15 g, 88%). Purification was achieved by dissolving the solid in a minimum amount of warm methanol (15 mL) and subsequently layering the solution with diethyl ether (Et$_2$O) and storing the sample at -40 °C for 16 h. The combined 1st and 2nd crops yielded 1.65 g of a white crystalline solid after drying under vacuum (total yield 67.5%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 8.98 – 8.91 (m, 2 H), 8.12 (tt, *J* = 7.8, 2.3 Hz, 2 H), 7.77 (ddd, *J* = 7.9, 3.0, 1.9 Hz, 2 H), 7.63 – 7.54 (m, 2 H), 6.31 (d, *J* = 4.6 Hz, 2 H), 4.60 (dd, *J* = 9.9, 4.6 Hz, 2 H), 4.48 – 4.40 (m, 2 H), 4.29 (s, OH), 3.92 (d, *J* = 5.0 Hz, 2 H). ^{13}C{^{1}H} NMR (126 MHz, CD$_3$CN): δ 195.15 (CO), 194.78 (CO), 153.63 (C$_{Py}$), 141.77 (C$_{Py}$), 128.54 (C$_{Py}$), 126.63 (C$_{Py}$), 102.26 (CH), 80.23 (CH$_2$), 73.67 (CH$_2$), 69.54 (CH$_2$OH). ESI-MS (pos. ion) m/z calcd for (**1**) [M$^+$]: 569.56. Found: 569.1 (M$^+$). Anal Calcd(found) for $C_{19}H_{17}BrN_3O_6Re$: 35.14 (35.38) %C, 2.64 (2.53) %H, 6.47 (6.67) %N.

3.3 Synthesis of *fac*-Re(L1^{meso-H})(CO)$_3$ (10).

In a glove box under N$_2$ atmosphere, a 100-mL Schlenk flask was charged with **8** (298 mg, 0.458 mmol), CsOH·H$_2$O (155 mg, 0.924 mmol, 2.02 equiv), and a Teflon-coated stir bar. THF (15 mL) was added and the mixture was stirred rapidly. After 24 h of stirring at 22 °C, precipitates were removed by filtration through a Teflon-syringe filter. The golden-yellow filtrate was concentrated in vacuo to its saturation point of approximately 10 mL. Hexanes (1.5 mL) were layered onto the solution and the vial was stored at -20 ºC. After 2 days, a powder was collected by suction filtration and dried in vacuo (yield 174 mg, 59.3%). ^{1}H NMR (500 MHz, THF-*d*$_8$): δ 8.65 (d, *J* = 5.5 Hz, 1 H), 8.47 (d, *J* = 4.8 Hz, 1 H), 8.05 (t, *J* = 7.9 Hz, 1 H), 7.87 (d, *J* = 4.8 Hz, 2 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.45 (t, *J* = 6.6 Hz, 1 H), 7.34 (q, *J* = 5.0 Hz, 1 H), 7.09 (s, 1 H), 5.56 (s, 1 H), 4.34 (d, *J* = 8.7 Hz, 1 H), 4.24 (d, *J* = 9.0 Hz, 1 H), 4.07 (d, *J* = 8.7 Hz, 1 H), 3.93 – 3.84 (m, 2 H), 3.48 (d, *J* = 9.1 Hz, 1 H). ^{13}C(^{1}H) NMR (126 MHz, CDCl$_3$): δ 161.18, 157.47, 152.62, 150.01, 140.73, 140.03, 137.66, 126.63, 125.70, 124.67, 100.68, 100.49, 81.59, 77.98, 75.66, 73.09. Calcd(found) for $C_{19}H_{17}BrN_3O_6Re$: 40.14 (39.44 %C, 2.84 (3.12) %H, 7.39 (7.21) %N.

3.4 Electrochemical Studies.

Cyclic voltammograms of **8** and **10** were examined in THF and acetonitrile solutions with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte under argon. A BASi Epsilon potentiostat was used with a C3 cell stand and 3mm glassy carbon working electrode, Pt wire counter electrode, and silver wire pseudo-reference electrode. Solutions of compounds **8** and **10** were prepared (1 mM) in air and degassed by purging with argon for 5 min prior to performing electrochemistry. Samples were reference to added ferrocene at the end of the experiment. For experiments with CO$_2$, the Ar purge/blanket gas was replaced with CO$_2$. For the bulk electrolysis, a cell was made using a 5 mL r.b. flask sealed with a septum through which wires were passed and attached to 5 mm x 5 mm x 8mm carbon foam electrodes (McMaster-Carr #3947K11). The analyte solution was added via syringe to the closed flask, and the flask purged with CO$_2$. CPE was carried out at -2.9 V for 60 min. The gas above the solution was analyzed for CO by GC (HP-Molesieve column, 30 m x 0.53 mm bore, 50µm film, 70 °C). 200 µL methane was added as internal standard. A standard gas mixture of 20 mL methane plus 20 mL CO in 500 mL CO$_2$ was prepared and used for calibration and CO quantification. No hydrogen was observed by GC.

4. CONCLUSIONS

Two novel rhenium complexes bearing a known fused oxazolidine ligand have been prepared and structurally characterized. The ligand, ((3*R*,5*S*,7a*s*)-3,5-di(pyridin-2-yl)-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazol-7a(7*H*)-yl)methanol (**L1^{meso}**) adopted either a κ^3–*NNN* binding mode in the case of complex **8**, or a κ^3–*ONN* binding mode as in **10**. The versatility of the ligand in coordination chemistry is well-established, although this is the first instance in which κ^3–*ONN* coordination of the deprotonated *syn* meso diastereomer has been observed. Loss of CO from this compound proved difficult, impeding further reactivity studies. Future work will be undertaken to determine the catalytic activity of these complexes in the reduction of CO$_2$ and coupling of alcohols similarly to **1**, **2**, and **3**, as well as the dehydrogenation of alcohols. Given that **8** and **10** lack a central N-atom capable of accepting a proton from substrate, which is of demonstrated importance in prior studies, external H-atom acceptors may be necessitated in these screenings. However, it is possible for the coordinated oxygen atom in **10** to accept a proton in a concerted metalation-deprotonation (CMD) event.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Supporting_Information. Includes NMR spectra and details of the X-ray structures of **8** and **10** (two polymorphs). These data are available from the Cambridge Structural Database (CCDC #2262446-2262448). See DOI: 10.1039/x0xx00000x

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